

PATENT SPECIFICATION

(11) 1202687

1202687

NO DRAWINGS

- (21) Application No. 13102/69 (22) Filed 12 March 1969
- (31) Convention Application No. 828971 (32) Filed 28 March 1968 in
- (33) Italy (IT)
- (45) Complete Specification published 19 Aug. 1970
- (51) International Classification C 07 c 37/08 49/08
- (52) Index at acceptance

C2C 3A13B2A1 3A13B2F3 3A14A1A 3A14A7C



(54) PROCESS FOR PREPARING PHENOL AND ACETONE

(71) We, SOCIETA' ITALIANA RESINE S.P.A., an Italian Joint Stock Company, of 33 Via Grazioli, Milan, Italy, do hereby declare the invention, for which we pray that 5 a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an improved process for preparing phenol and acetone by the acid decomposition of cumene hydroperoxide.

It is known that cumene hydroperoxide is obtained by the oxidation of cumene ($C_6H_5CH(CH_3)_2$) by means of oxygen or oxygen-containing gases in a liquid phase, usually in the presence of catalysts.

With these processes cumene is only partially converted (usually by 20 to 50%) and in addition to cumene hydroperoxide more or less large quantities of by-products such as acetophenone, and more particularly dimethylphenylcarbinol, are formed.

A number of processes known at present, which utilize sulphuric acid for the acid decomposition of cumene hydroperoxide in preparing phenol and acetone, suffer from the drawback of yielding rather large quantities of cumylphenols and compounds of a pitchy character.

30 The formation of such undesirable side products is believed to be attributable to the condensing and dehydrating action of sulphuric acid. However the process may be explained, the formation of by-products leads to a lower phenol and acetone output.

An object of the invention is to provide a process for the acid decomposition of cumene hydroperoxide which, by producing smaller quantities of by-products than in the prior art, affords a higher yield of phenol and acetone.

According to the process of the invention, cumene hydroperoxide, of purity at least 70 weight %, the remainder being essentially

cumene, is reacted in a decomposition reactor at a temperature of 30° to 70°C with acetone and an aqueous solution of sulphuric acid of concentration 10—75 weight %, the acid being used in such an amount that the reaction product discharged from the reactor contains 0.05 to 1.0 weight % of sulphuric acid and the acetone being used in such an amount that the reaction product contains 37 to 48 weight % acetone.

In one way of carrying out the method of the invention, the sulphuric acid, acetone and cumene hydroperoxide are continuously fed into a reaction vessel, heating is applied to initiate the reaction, the reactor is cooled to keep the contents at a temperature of 30° to 70°C, and the reaction product is continuously withdrawn.

The process of the invention surprisingly substantially reduces the quantities of cumylphenol and pitch formed, presumably because under the aforesaid conditions the condensing action of sulphuric acid is restrained. This affords the advantages of a higher phenol and acetone yield, and the alphamethylstyrene formed at the decomposition stage may be recovered at a subsequent stage and recycled after hydrogenation to cumene.

The cumene hydroperoxide useful for the purposes of the invention may be obtained by the oxidation of cumene, in the liquid phase in a homogeneous medium or in an aqueous emulsion, by means of oxygen or a gas containing molecular oxygen, in the presence of small quantities of added substances such as caustic soda, sodium carbonate or calcium carbonate. The oxidation is normally carried out at a pressure of a few atmospheres and temperatures between 80° and 120°C. approximately.

According to a preferred embodiment the oxidation is carried out in a homogeneous medium utilizing the sodium salt of cumene hydroperoxide as an oxidation accelerator,

45

50

55

60

65

70

75

80

85

as this affords high reaction rates and a relatively small quantity of by-products when the cumene hydroperoxide content in the oxidation product amounts to about 20 to 50% by weight. The oxidation product is then evaporated in vacuum, such as in a thin film evaporator, to obtain a composition containing 70% or more by weight cumene hydroperoxide. These compositions are suitable to be fed together with acetone and aqueous sulphuric acid to the decomposition reactor, as described above.

In carrying out the invention the temperature is maintained during decomposition of cumene hydroperoxide at 30° to 70° C, preferably 45° to 55°C. At temperatures below 30° the decomposition rates are not high enough, whereas temperatures above 70°C result in the disadvantageous effects of the sulphuric acid as previously described. The reaction is exothermic and, after initial heating to cause the reaction to commence, cooling is generally required to keep the temperature of the reaction mixture within these limits.

With sulphuric acid concentrations exceeding 75% by weight the above described undesirable effects result, whereas with concentrations below 10% by weight the rate of the decomposition reaction is too slow.

No appreciable advantage derives from acetone contents exceeding 48% by weight, whereas contents below 37% by weight exhibit the condensing effects of the sulphuric acid as described above.

In a continuous process, part of the acetone obtained after separation from the de-

composition products, from which the acid catalyst has been removed, may be usefully recycled to the decomposition reactor.

The following examples illustrate the invention.

EXAMPLE 1

A 3 liter, jacketed glass reactor was employed, which was equipped with a stirrer, a thermometer for controlling the temperature, a reflux cooler, three inlets for charging cumene hydroperoxide, sulphuric acid and acetone, respectively, and with means for withdrawal of the reaction products.

The reactor was fed with the decomposition products from a preceding test, having a sulphuric acid content of 0.15% by weight. The mixture was heated with stirring to 50°C, the feed being then started with acetone, cumene hydroperoxide titrating 75% by weight and aqueous sulphuric acid of 75% by weight concentration, through their respective inlets.

At the time the feed of the reagents was started cooling water was admitted to the jacket in order to maintain the reaction mass at about 50°C, the feed of the reagents being adjusted so that the reaction products had an acetone content of 45% by weight and a sulphuric acid content of about 0.15% by weight.

The products delivered by the reactor were cooled to 25°C and neutralized by means of calcium carbonate. The salt which had separated was filtered off, the reaction liquid being distilled to separate its various fractions.

The results of analysis of various samples are as follows:

75	Phenol yield acetone yield pitch and cumylphenol	: 94.5% : 92.9% : 5.6% with respect to phenol.
----	--	--

EXAMPLE 2

The procedure as described in Example 1 was repeated, using 25% by weight aqueous sulphuric acid instead of 75%. The conditions were again so adjusted as to maintain

an acetone content in the decomposition products of 45% by weight and a sulphuric acid content of 0.15% by weight.

The results were as follows:

	Phenol yield acetone yield pitch and cumyl phenol	: 95.8% : 94.2% : 3.9% with respect to phenol.
--	---	--

Comparative Example 3

This example was carried out by feeding to the oxidation reactor aqueous 75% sulphuric acid and 75% cumene hydroperoxide.

No acetone was supplied; the remaining conditions were the same as in Example 1, the decomposition products having an acid content of 0.15% by weight.

The results were as follows:

100	Phenol yield acetone yield pitch and cumyl phenol	: 89.5% : 88.0% : 15.4% with respect to phenol.
-----	---	---

Comparative Example 4

This example was carried out under the same conditions as Example 1, with the dif-

ference that 100% sulphuric acid was supplied.

5

The results were as follows:

Phenol yield	: 91.5% by weight
acetone yield	: 90.2% by weight
pitch and cumylphenols	: 10.3% with respect to phenol

- 10 It is seen from Examples 3 and 4 that when no acetone is used, or sulphuric acid of concentration more than 75 weight %, the amounts of pitch and cumyl phenol formed are much increased.
- 15 **WHAT WE CLAIM IS:—**
1. A process for preparing phenol and acetone by acid decomposition of cumene hydroperoxide, wherein cumene hydroperoxide, of purity at least 70 weight %, the remainder being essentially cumene, is reacted in a decomposition reactor at 30° to 70°C with acetone and aqueous 10—75 weight % sulphuric acid, the acid being used in such an amount that the reaction product discharged from the reactor contains 0.05 to 1.0 weight % of sulphuric acid and the acetone being used in such amount that the reaction product discharged from the reactor contains 37 to 48 weight % acetone.
- 20 2. A process as claimed in claim 1, wherein the sulphuric acid, acetone and cumene hydroperoxide are continuously fed into a reaction vessel, heating is applied to initiate the reaction, the reactor is cooled to keep the contents at a temperature of 30° to 70°C,
- 25
- 30
- 35

and the reaction product is continuously withdrawn.

3. A process as claimed in claim 1 or 2, wherein the temperature of the reaction mixture is maintained at 45° to 55°C.

4. A process as claimed in any of the preceding claims, wherein the cumene hydroperoxide is prepared by the oxidation of cumene by oxygen or a gas containing molecular oxygen, and the oxidation product is evaporated in vacuum to obtain a product containing at least 70 weight % cumene hydroperoxide.

5. A process for preparing phenol and acetone as claimed in claim 1, substantially as herein described in Example 1 or 2.

6. Phenol and acetone, when prepared by a process as claimed in any of the preceding claims.

H. D. FITZPATRICK & CO.,
Chartered Patent Agents,
27, Chancery Lane,
London, W.C.2,
and
14—18, Cadogan Street,
Glasgow, C.2.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1970.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY. from
which copies may be obtained.